Microstructural Characterization of PEM Fuel Cell MEAs

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May 15, 2007

Project ID FC3

Project Overview

Timeline

- Project initiated in FY2000
- Continuous - fundamental research on microstructural characterization to improve MEA durability

Barriers

- Fuel Cell Barriers Addressed
  - A: Durability
  - B: Cost
  - C: Performance

Budget

- Total Funding to date - ~$1.6M
- Funding in FY06 - $375k ($300k baseline project plus $75k project with Arkema)
- Funding in FY07 - $300k

Partners

- Los Alamos National Laboratory
- Argonne National Laboratory
- PlugPower
- Honda Research Institute
- Rensselaer Polytechnic Institute
- Arkema

ORNL Research Objectives

- Identify high-resolution imaging and compositional/chemical analysis techniques for characterization of the material constituents comprising PEM fuel cell MEAs
  - μm- to nm-scale using FEG-SEM
  - nm- to sub-angstrom scale imaging using TEM/STEM
  - Compositional analysis using TEM/STEM with EDS
  - Surface chemistry using XPS
- Apply these analytical and imaging techniques for the evaluation of microstructural and microchemical changes to MEA materials during life-testing
- Elucidate microstructure-related degradation mechanisms contributing to PEM fuel cell performance loss

Approach: Used Advanced Imaging and Compositional Analysis Techniques to Evaluate Atomic-Scale MEA Microstructures

- Develop innovative methodologies to prepare samples for microstructural analysis of MEA constituents
  - The use of "partial-embedding" for microtomy
  - Cryo-microtomy/cryo-transfer for membrane analysis in FEG-TEM
- Apply state-of-the-art electron microscopy techniques for the analysis of MEA materials
  - High-resolution FEG-SEM - Hitachi S4800
  - High-resolution FEG-TEM imaging (*nm-scale*) - Hitachi HF-2000
  - High-angle annular dark field (HAADF) imaging (Z-contrast imaging) in an aberration-corrected STEM (*sub-angstrom scale*) - JEOL 2200FS-AC
- Collaborate with industry, academia, and national laboratories to make these techniques (and expertise) available for MEA processing and/or life-testing studies

Technical Accomplishments and Progress ORNL/LANL Collaboration

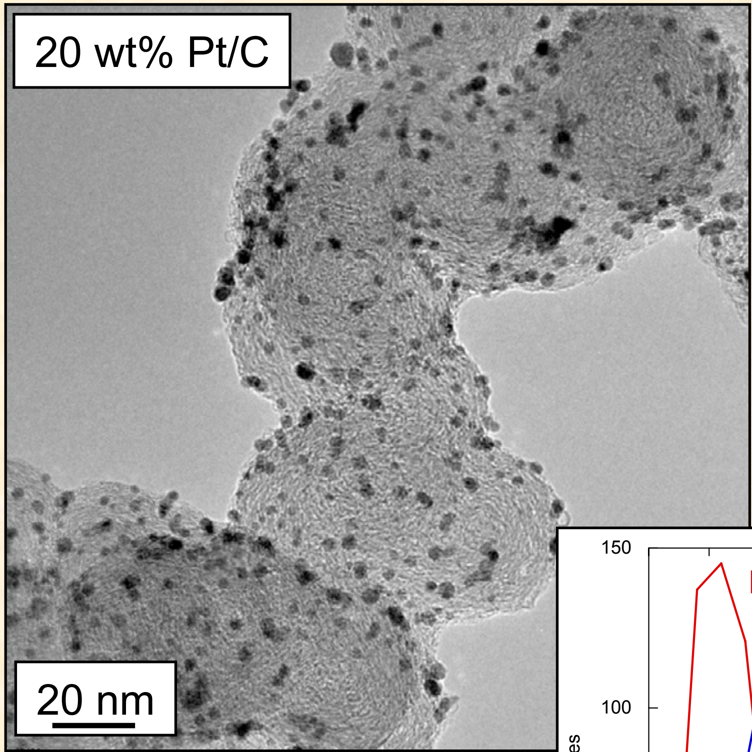
- Primary focus has been on characterization of an E-TEK 20 wt% Pt-Co (3:1) bimetallic catalyst
- As-received powder - Pt-Co on Vulcan XC-72
- Fresh MEA with Pt-Co/C cathode
- Same MEA aged to evaluate catalyst changes:
  - H_2/N_2 cycled 0.4-0.96 V @ 80°C, **100% RH**, ~35k cycles
  - H_2/N_2 cycled 0.4-0.96 V @ 80°C, **50% RH**, ~40k cycles
  - DOE drive cycle for 8905 cycles (results not complete)

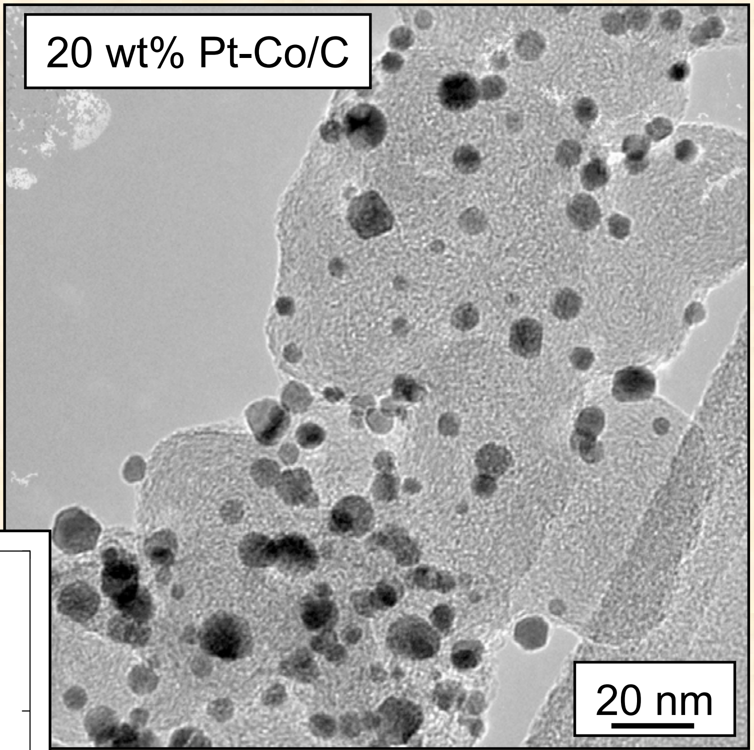
Bimetallic Catalysts are Being Evaluated to Replace Pt-only Catalysts

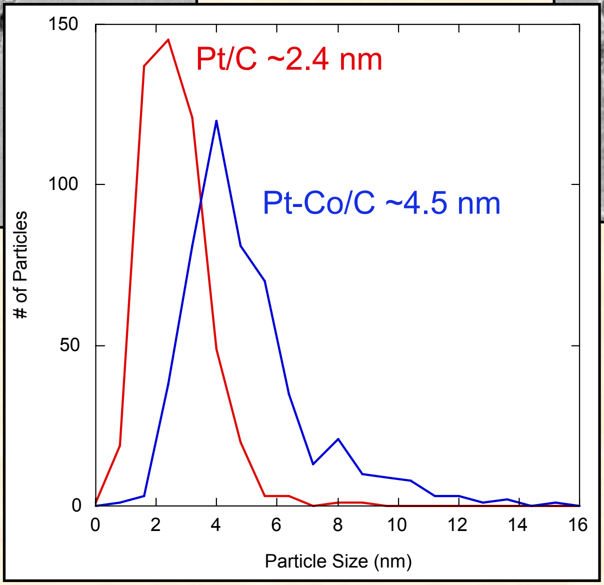
- Pt is expensive and supply is limited
- Pt alloyed with transition metals (M=Co, Ni, Cr) have shown enhanced catalytic activity compared with Pt
  - Changes in Pt-Pt and Pt-M bond lengths
  - Changes in atomic coordination/nearest neighbors
  - Electron density of states in Pt 5*d* orbital
  - Nature of surface
- Atomic ordering of the Pt alloys will enhance the catalytic activity
- Specific crystallographic planes/facets can enhance activity

References: Stamenkovic et al., *J. Phys. Chem. B* **106** (2002) 11970.
Xiong and Manthiram, *J. Mater. Chem*. **14** (2004) 1454.
Mun et al., *J. Chem. Phys.* **123** (2005) 204717.
Gasteiger et al., *Appl. Cat. B* **56** (2005) 9.
Xiong and Manthiram, *J. Electrochem. Soc.* **152**(4) (2005) A697.

Size and Size-Distribution Differences Between Pt and Pt-Co Catalyst Particles



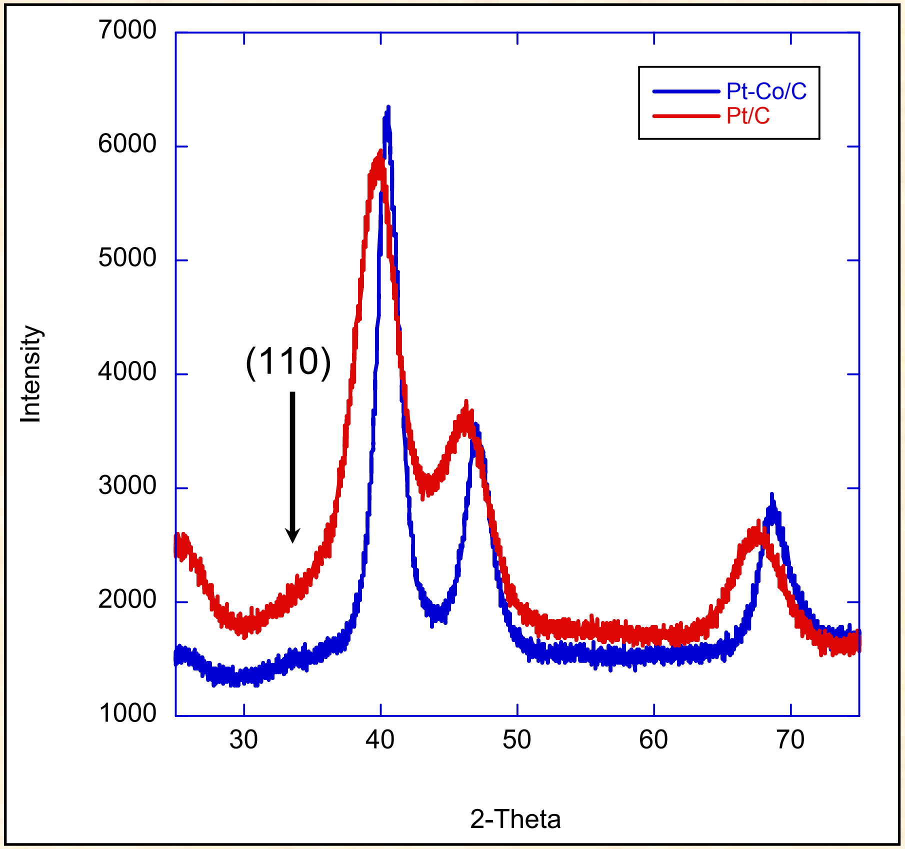




Composition of Pt-Co given as 3Pt:1Co

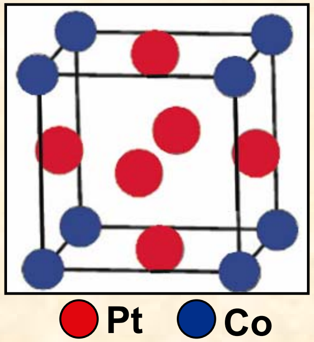
Actual bulk Pt-Co composition 6Pt:1Co

Crystal Structure of E-TEK 20 wt% Pt-Co/XC-72



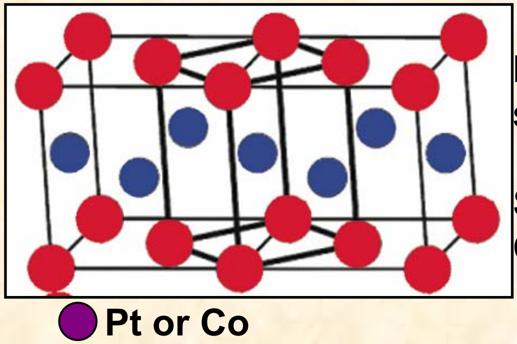
- XRD data shows larger Pt-Co particle size
- Shift to higher 2-theta indicates contraction of Pt lattice due to incorporation of Co
- Intensity of (110) superlattice reflection for Pt_3Co is very low - limited atomic ordering

Possible Pt-Co crystal structures:



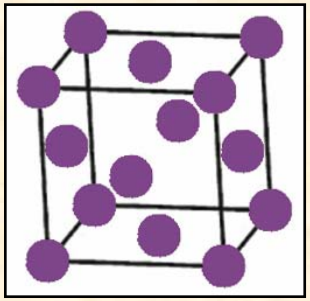
Pt_3Co - fully ordered $L1_2$ structure (fcc)

Stoichiometric = 9 wt% Co
Can have up to 15 wt% Co



PtCo - fully ordered $L1_0$ structure (tetragonal)

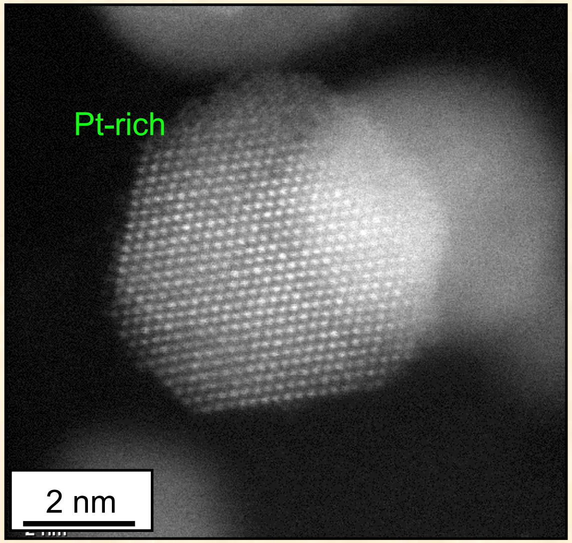
Stoichiometric = 23 wt% Co
Can have up to 40% wt% Co

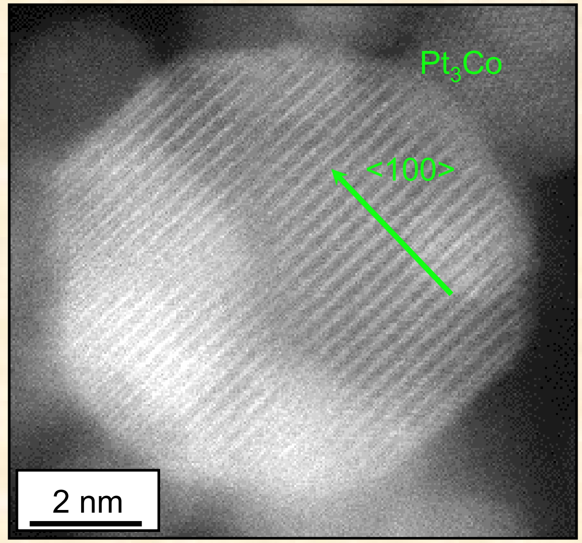


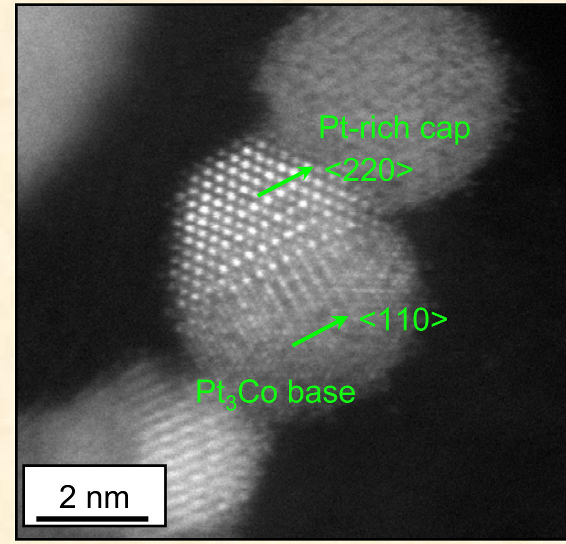
Pt-Co - disordered solid solution (fcc)

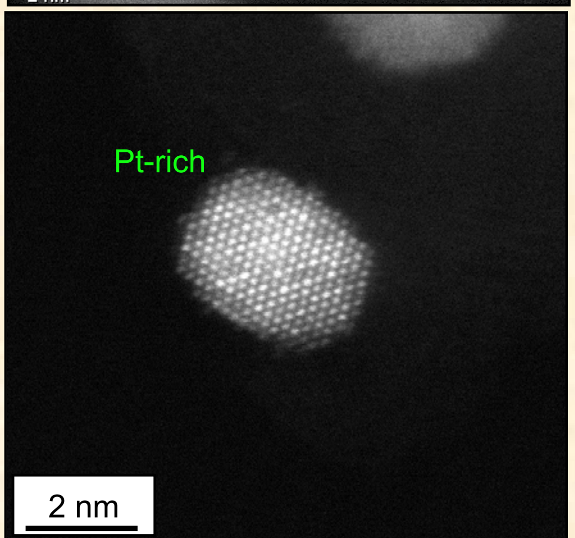
Can have up to 50 wt% Co

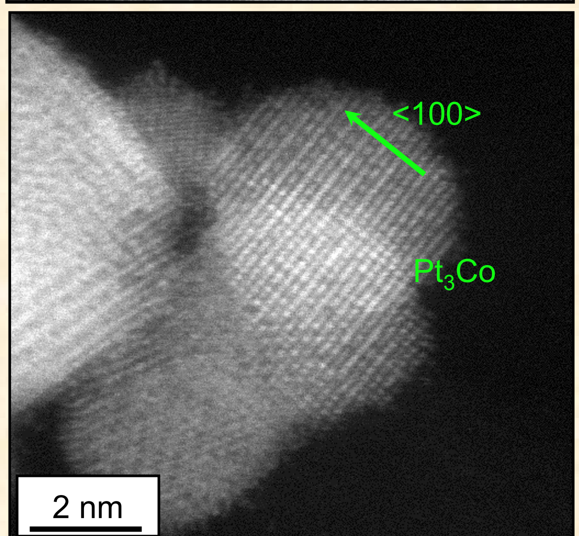
The Crystal Structure of Individual Pt-Co Particles Is Determined From HAADF-STEM Images







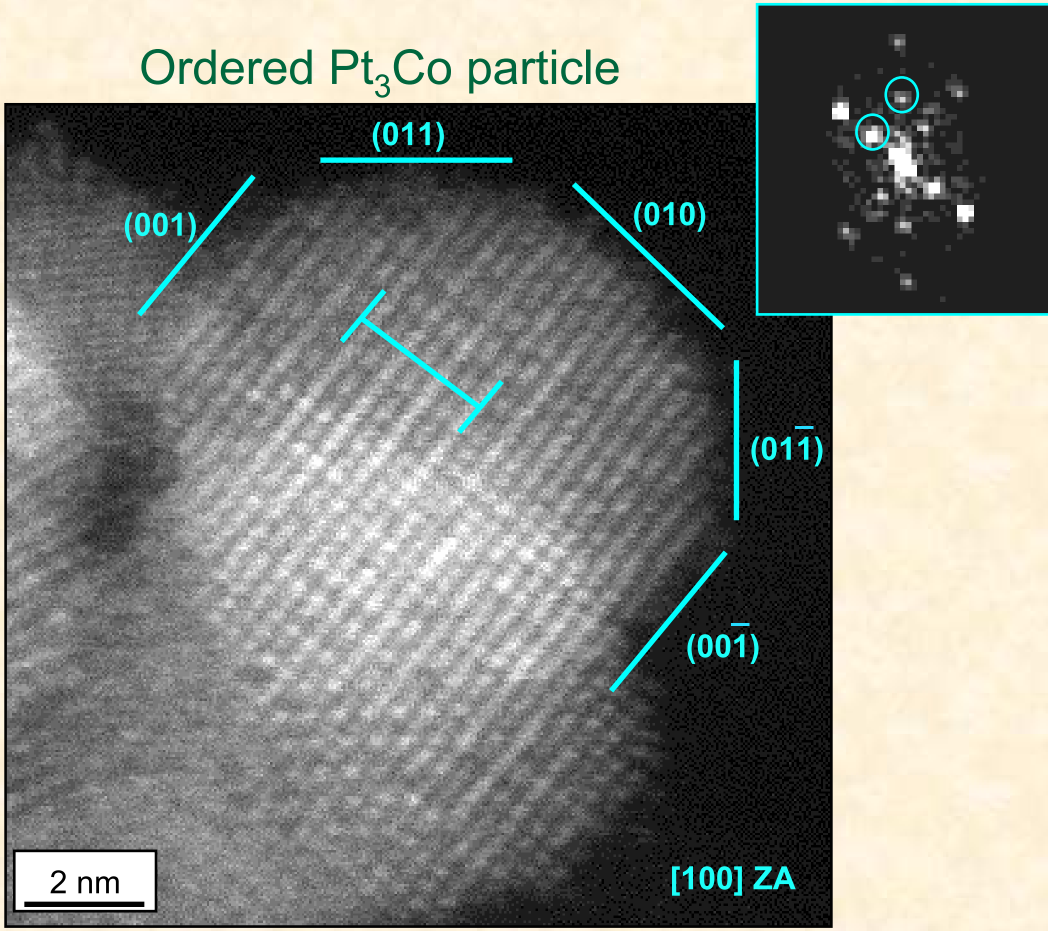


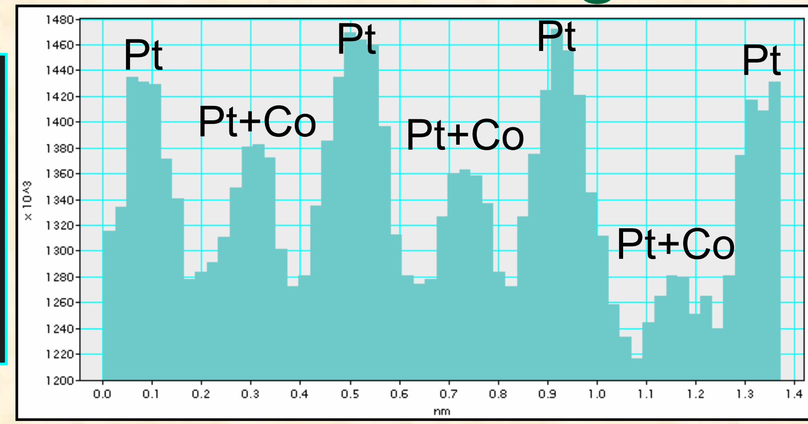


- Most of the small particles are Pt-rich (disordered alloy)
- Ordered particles of Pt_3Co identified
- Pt/Pt_3Co particles also prevalent

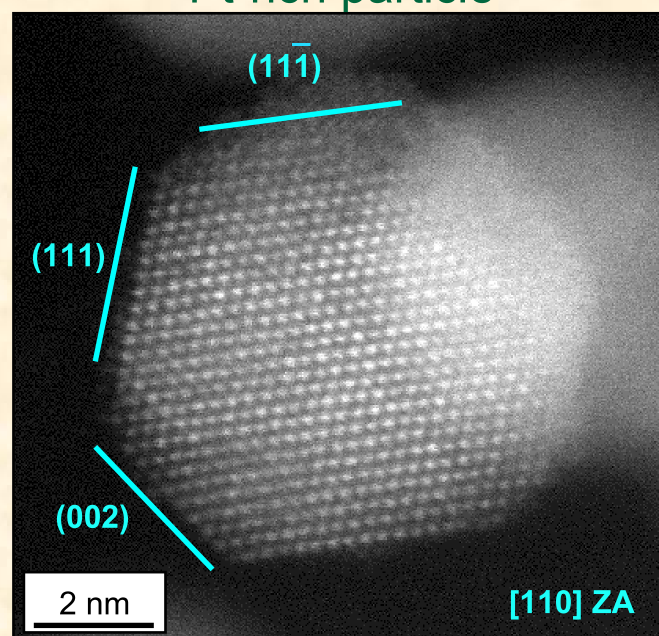
The Crystal Structure of Individual Pt-Co Particles Is Determined From HAADF-STEM Images

Ordered Pt_3Co particle



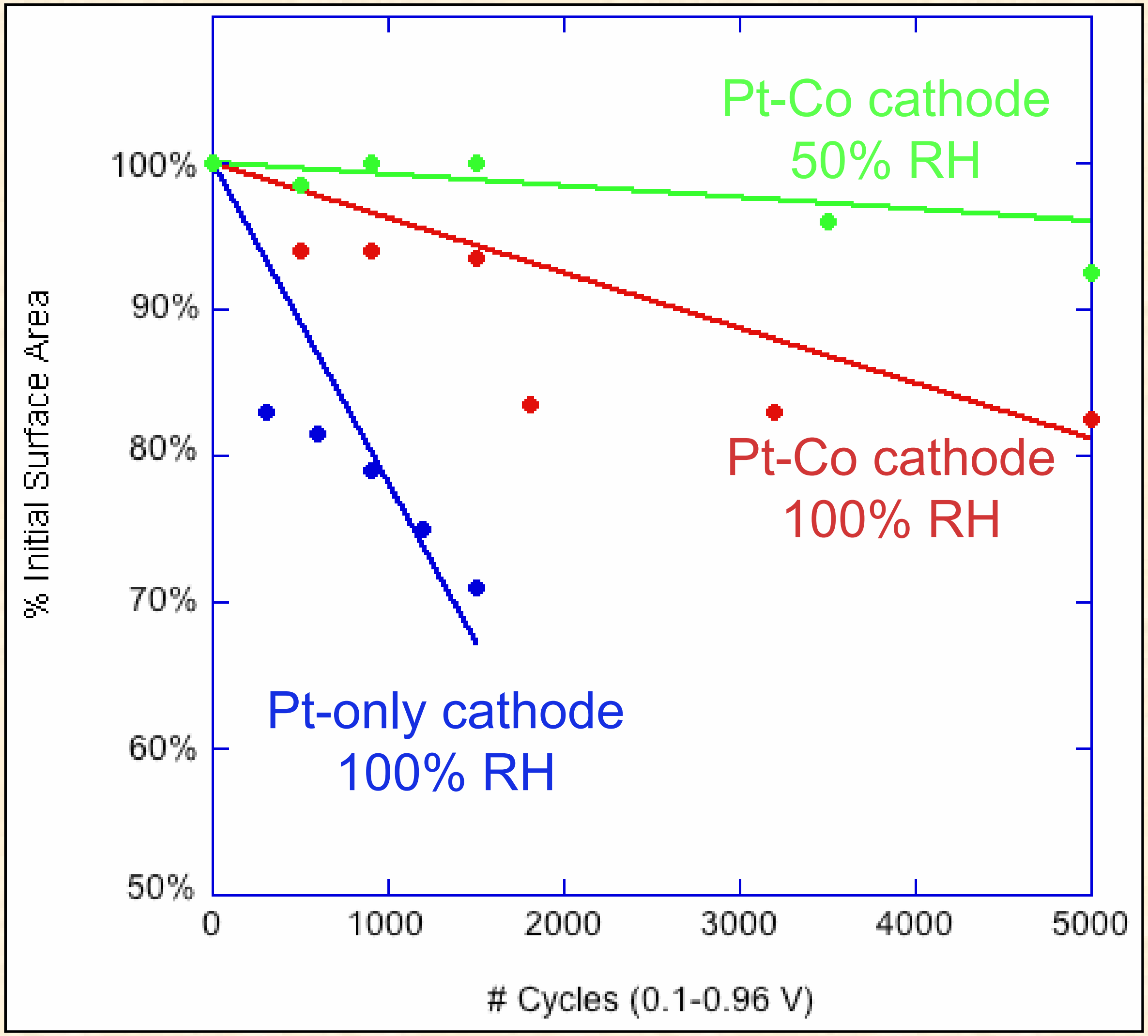


Pt-rich particle



{100} Pt better activity than {111} Pt

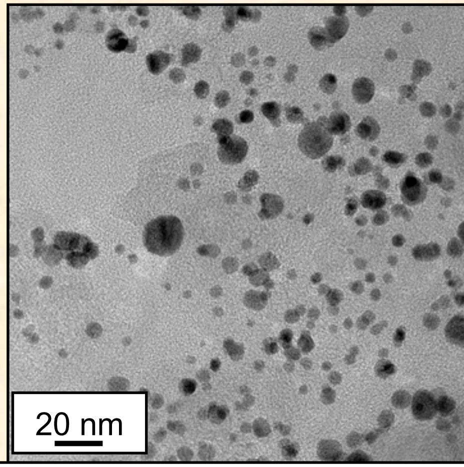
During H_2/N_2 Cycling (0.4-0.96 V) at 80°C, Loss Of EASA Observed for Pt-Co Cathode Catalysts



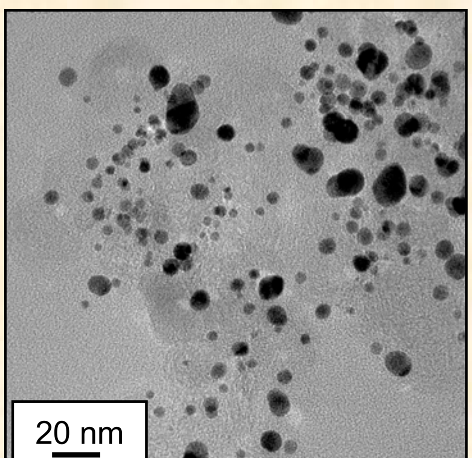
- Pt-Co exhibits lower loss of surface area compared with Pt during potential cycling
- Higher %RH enhances particle growth

Borup et al., 2006 DOE Hydrogen Program Review, FC28 for Pt results.

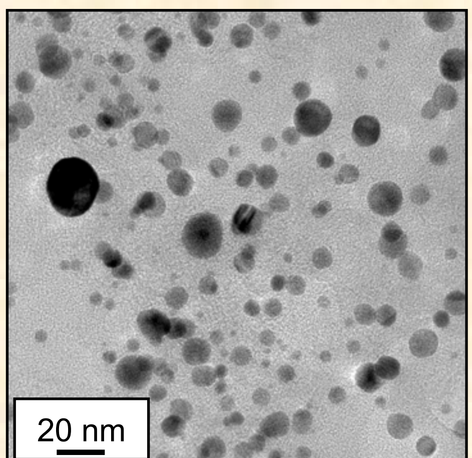
During H_2/N_2 Cycling (0.1-0.96 V), Growth of Pt-Co Particles Is Quantified *f*(%RH) by TEM



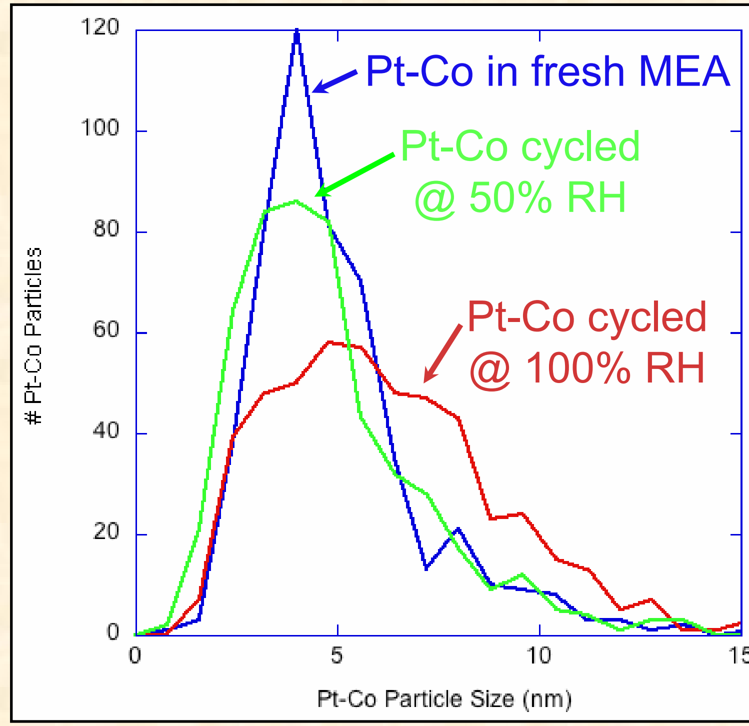
Pt-Co particles in fresh MEA cathode



Pt-Co ~40k cycles @ **50% RH**

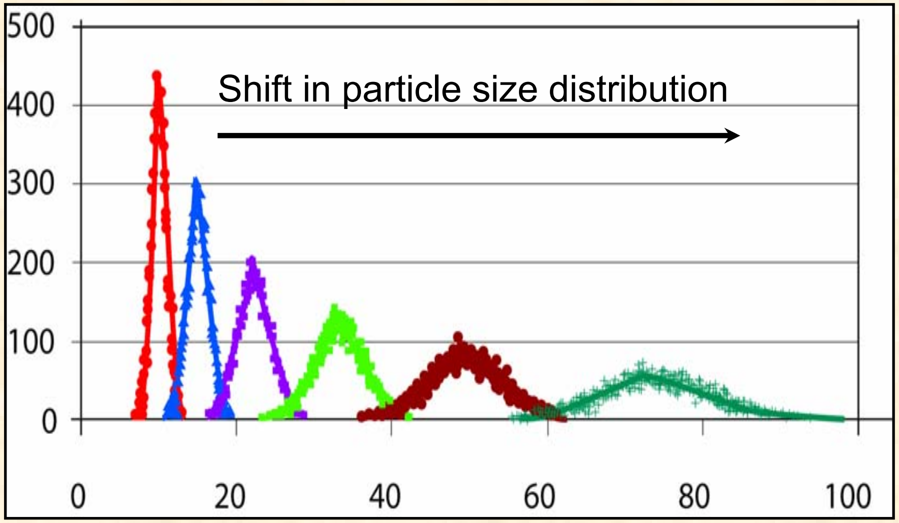


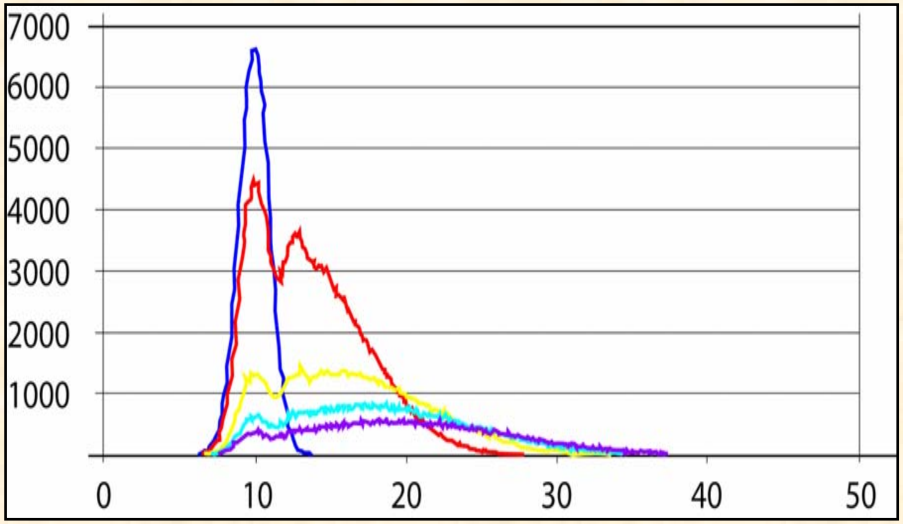
Pt-Co ~36k cycles @ **100% RH**



There is a change in the form of the Pt-Co particle size distribution, which is more pronounced following cycling at 100% RH.

During H_2/N_2 Cycling (0.4-0.96 V), Growth of Pt-Co Particles Occurs Via Combined Mechanisms: Dissolution-Reprecipitation and Coalescence





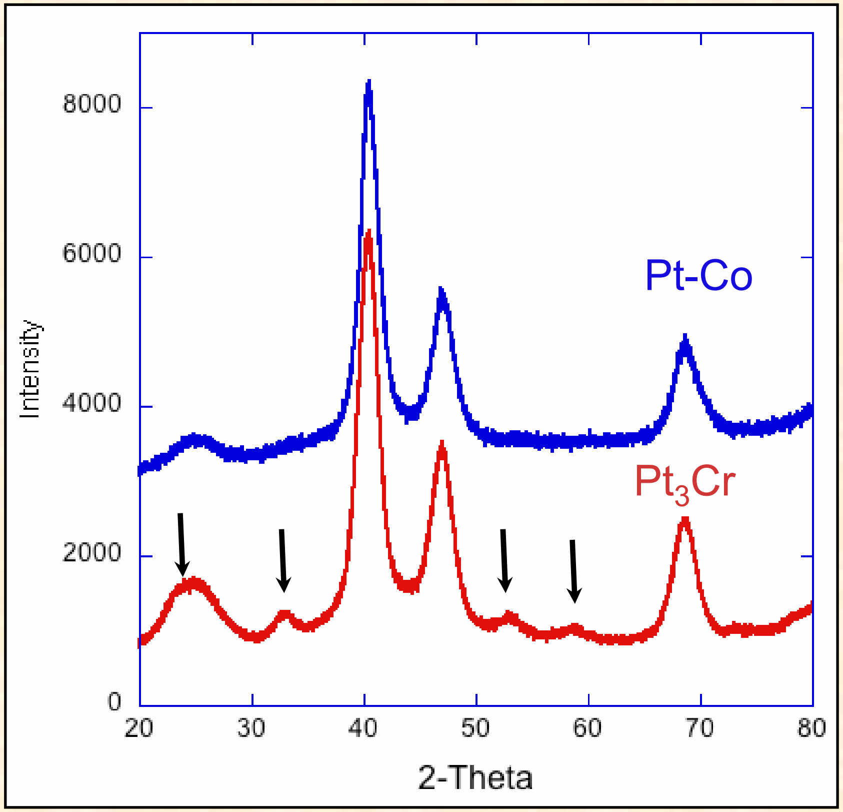
Typical particle growth associated with an Ostwald Ripening process - large particles grow at the expense of small particles such that surface energy is reduced.

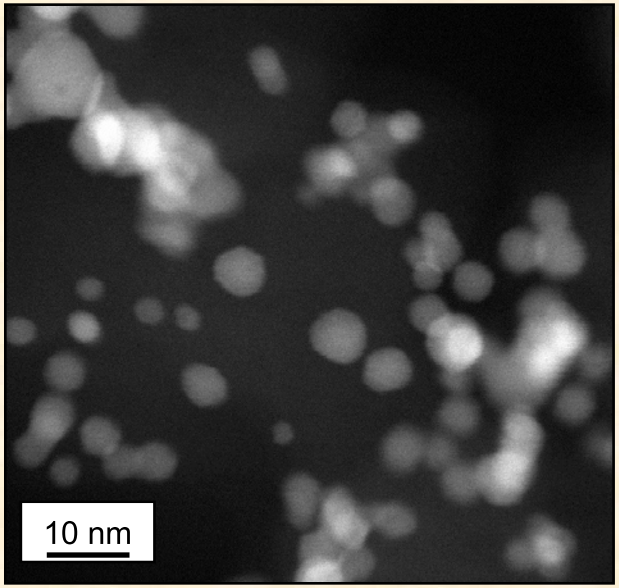
Size distribution shift from narrow distribution of small particles to wider distribution of larger particles

Kinetic particle growth associated with combined mechanisms of dissolution-reprecipitation and particle coalescence.

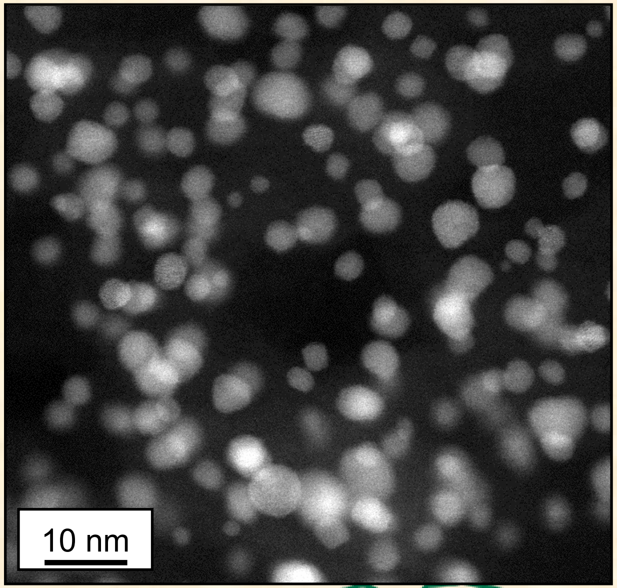
More gradual size distribution change from a narrow distribution of small particles to a bimodal particle size distribution that includes small and large particles

What About Other Ordered Bimetallic Catalysts?





Pt-Co particles

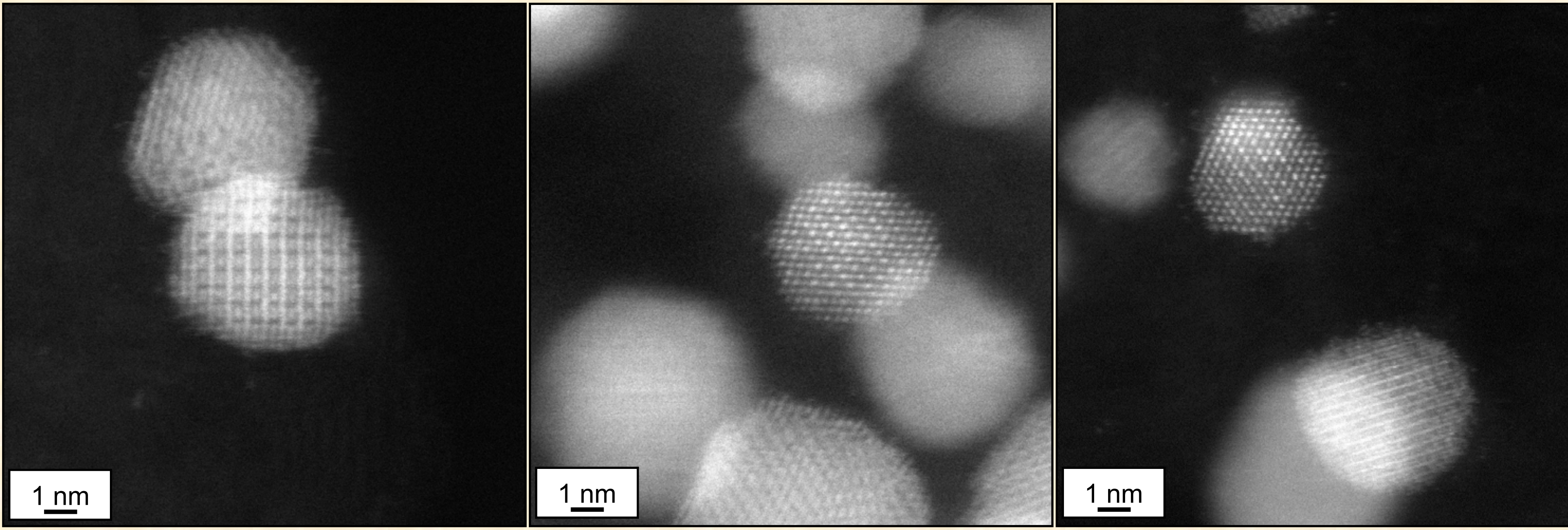


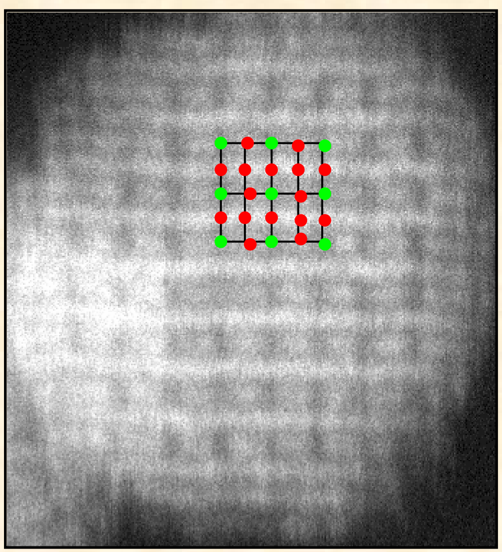
Pt_3Cr particles

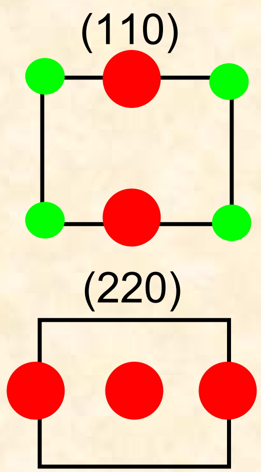
XRD data clearly shows superlattice reflections for Pt_3Cr particles and smaller average particle size

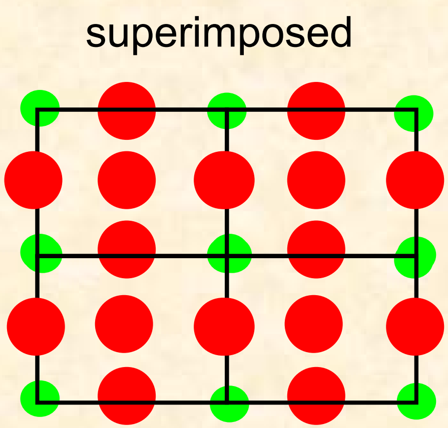
STEM shows differences in particle size distributions between Pt-Co and Pt_3Cr

Unlike Pt-Co Catalyst, All Pt_3Cr Particles Ordered





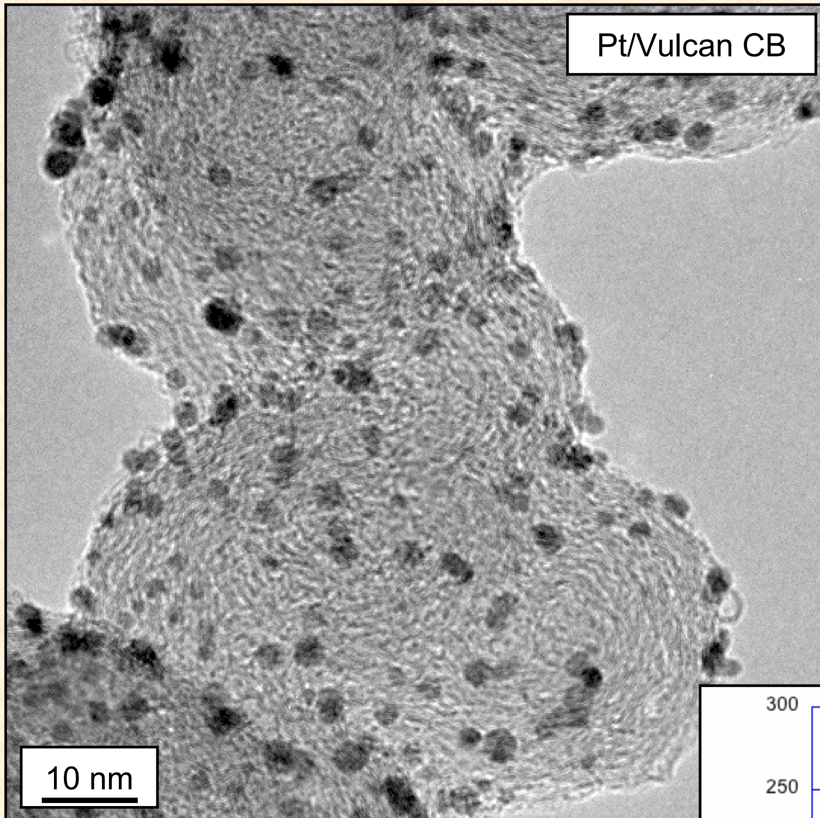


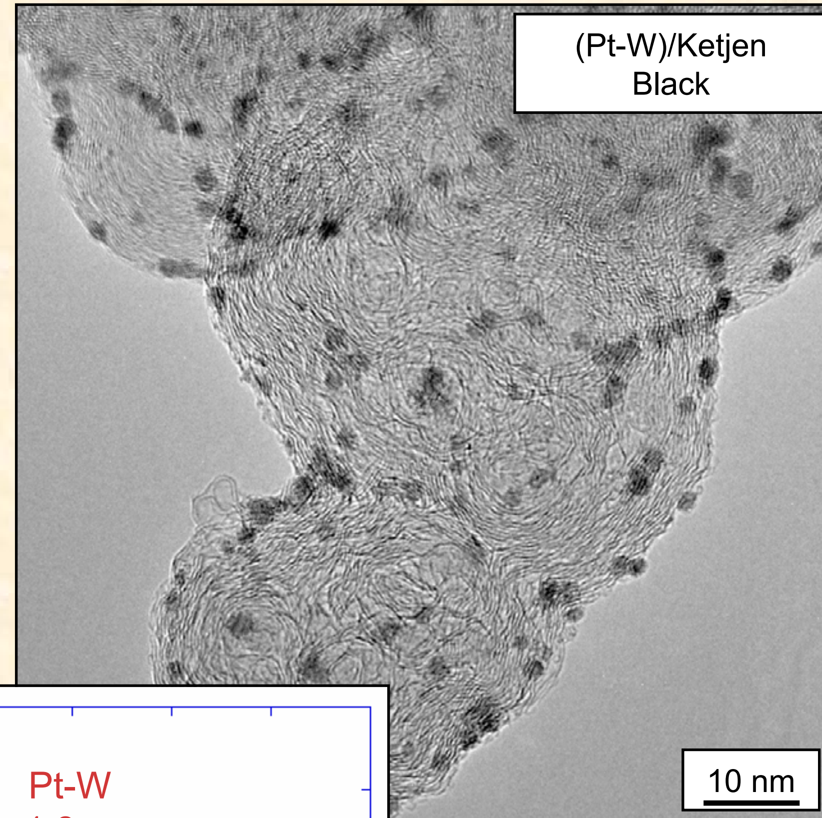


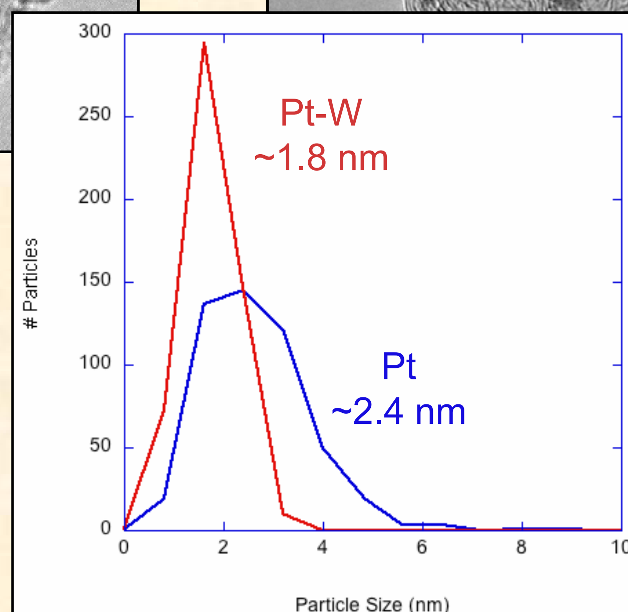
Pt atoms face-centers

Co atoms at corners

Many Pt-Based Bimetallic Particles Exhibit No Order

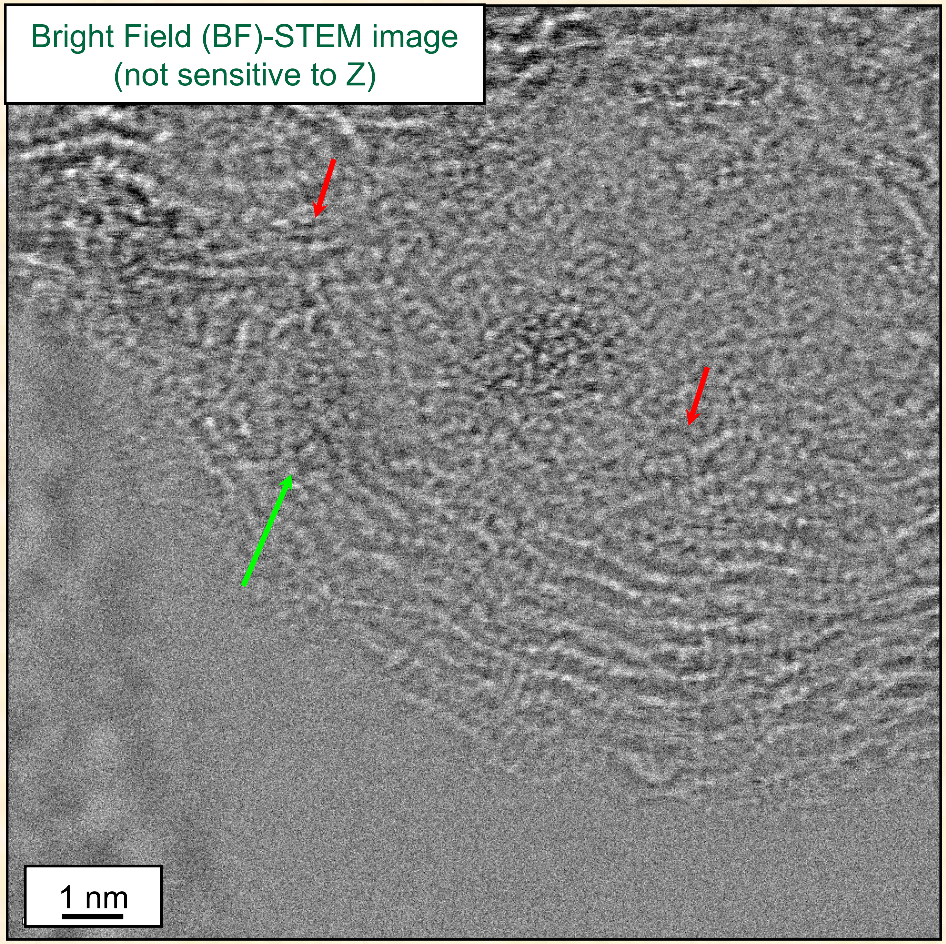


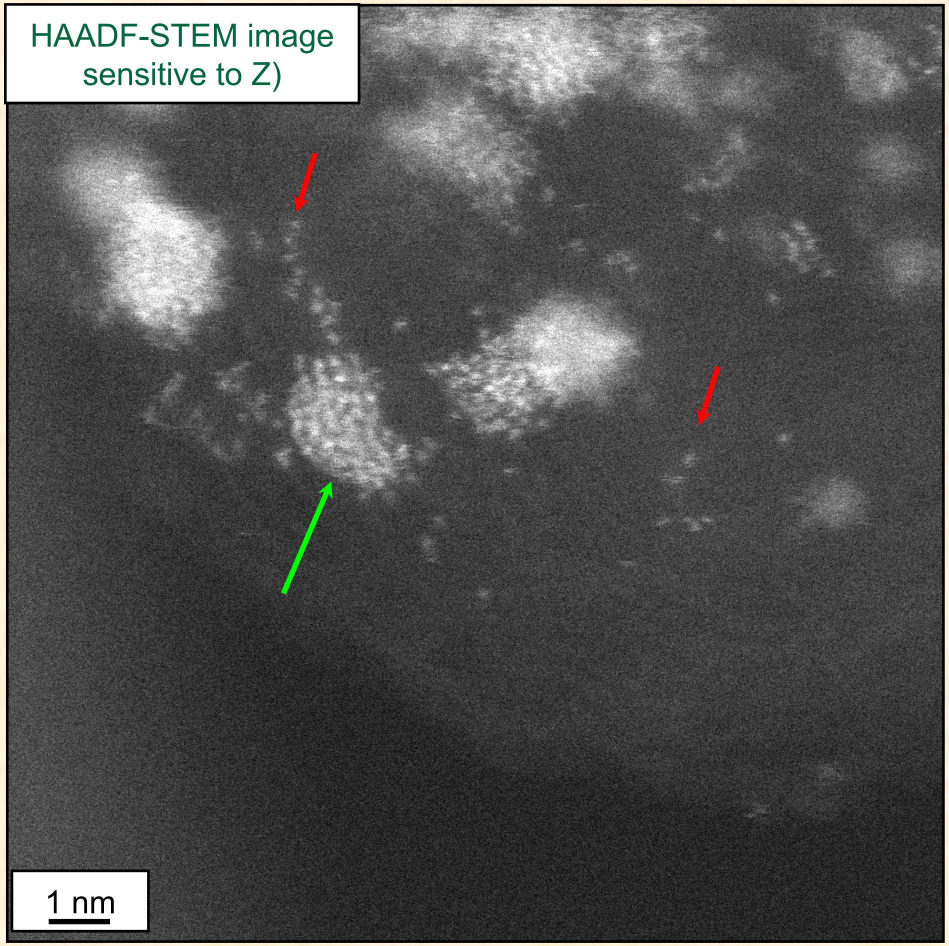




Composition of Pt-W particles ranged from ~50-70 at% W (nominal 43Pt-57W)

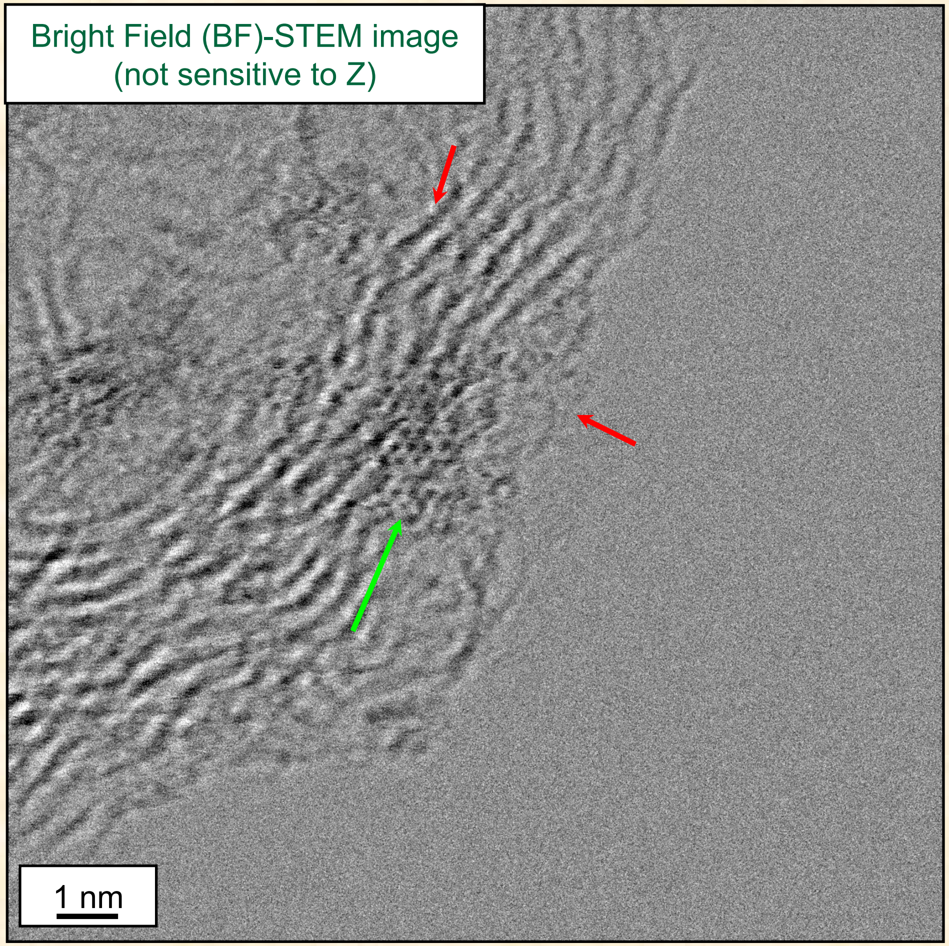
Pt-W "Assembles" Into Particles That Are Not Always Crystalline - Pt Atoms Cover Surface of KB Support

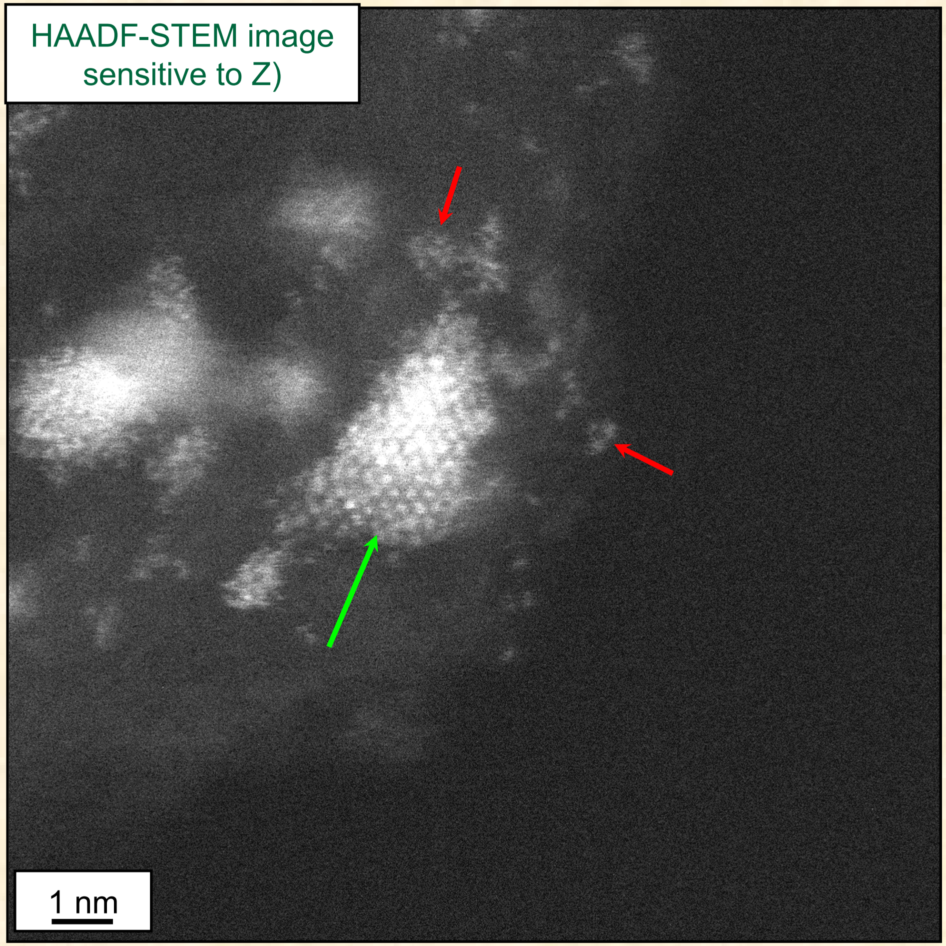




Note that individual, non-assembled Pt and/or M species on the carbon surface were not observed for highly crystalline, ordered bimetallic catalysts (Pt-Co or Pt-Cr systems)

Pt-W "Assembles" Into Particles That Are Not Always Crystalline - Pt Atoms Cover Surface of KB Support





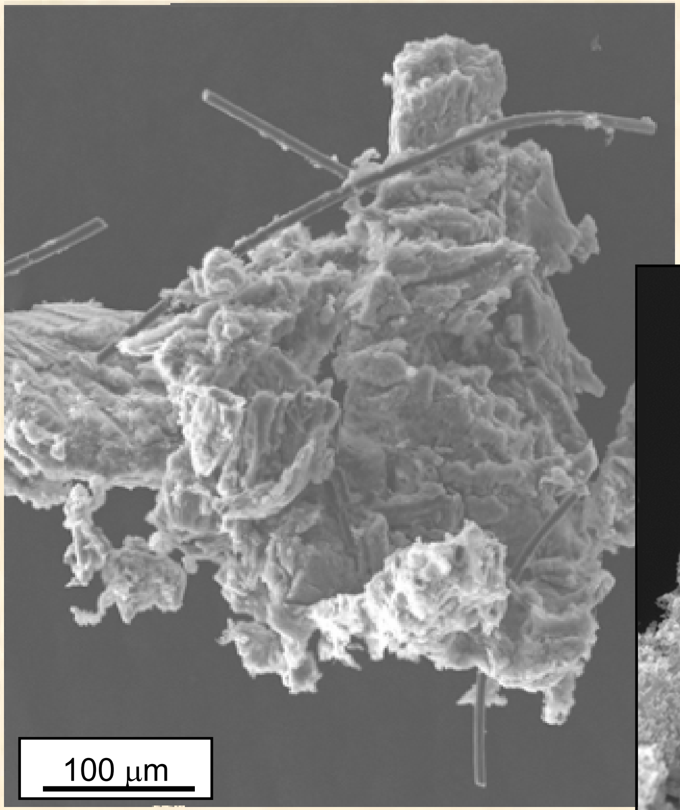
Note that individual, non-assembled Pt and/or M species on the carbon surface were not observed for highly crystalline, ordered bimetallic catalysts (Pt-Co or Pt-Cr systems)

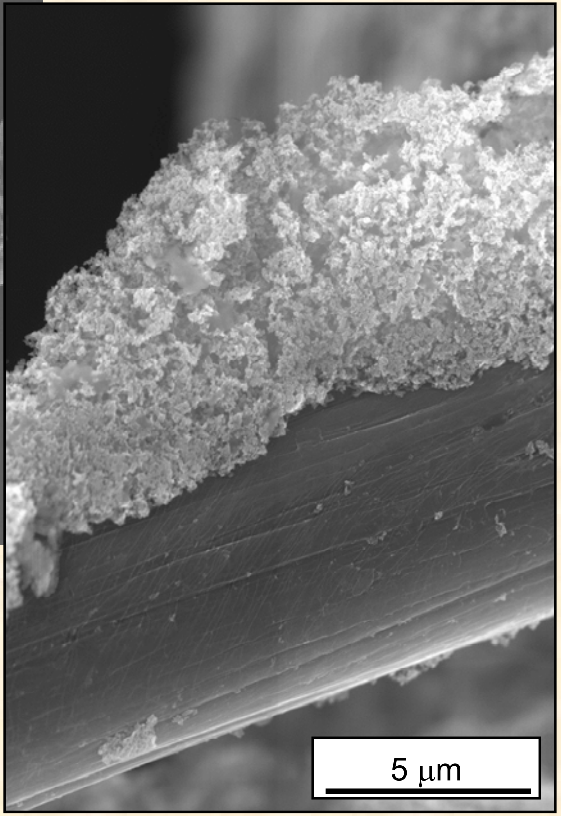
Technical Accomplishments and Progress ORNL/ANL Collaboration

10 wt% Pt/Vulcan imbibed with Nafion solution -supported on carbon fiber cloth

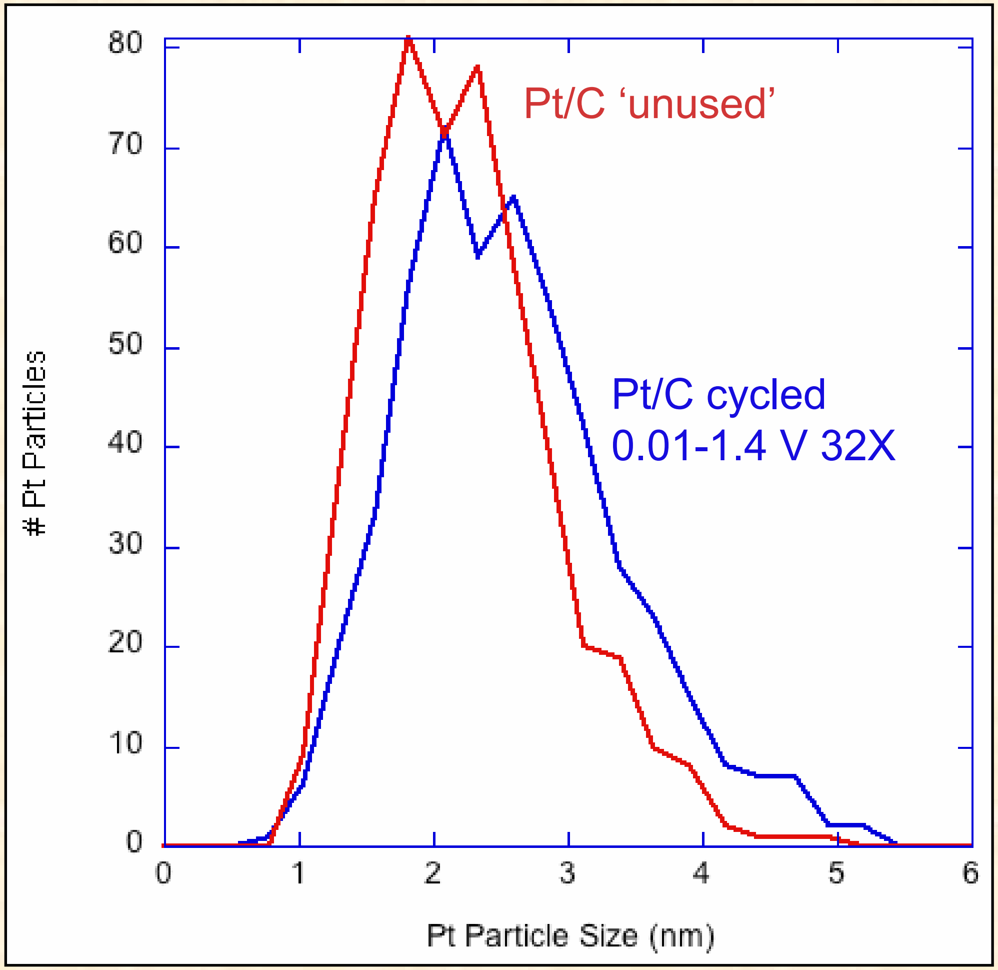
- cycled 32 times (0.01-1.4V) in 0.6 M perchloric acid electrolyte
- cycled (as above) then held 72h at 1.1 V (vs. RHE)
- cycled (as above) then held 72h at 1.2 V (vs. RHE)

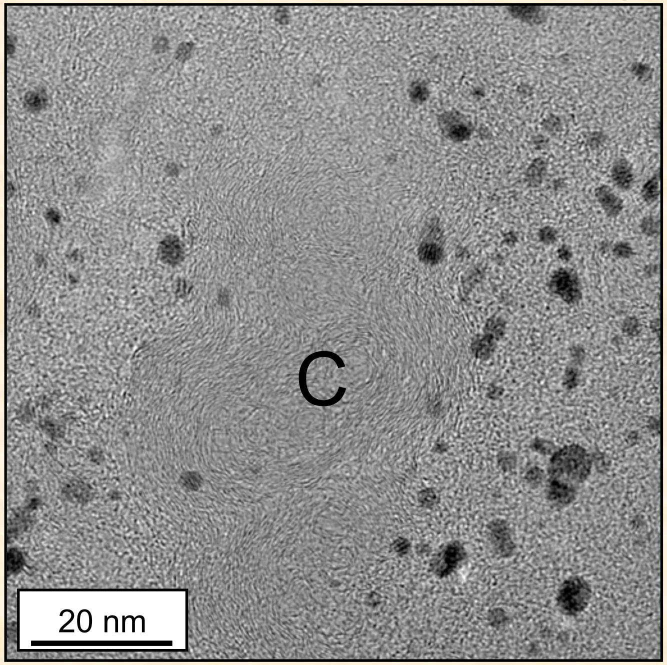
Interested in Pt particle size changes





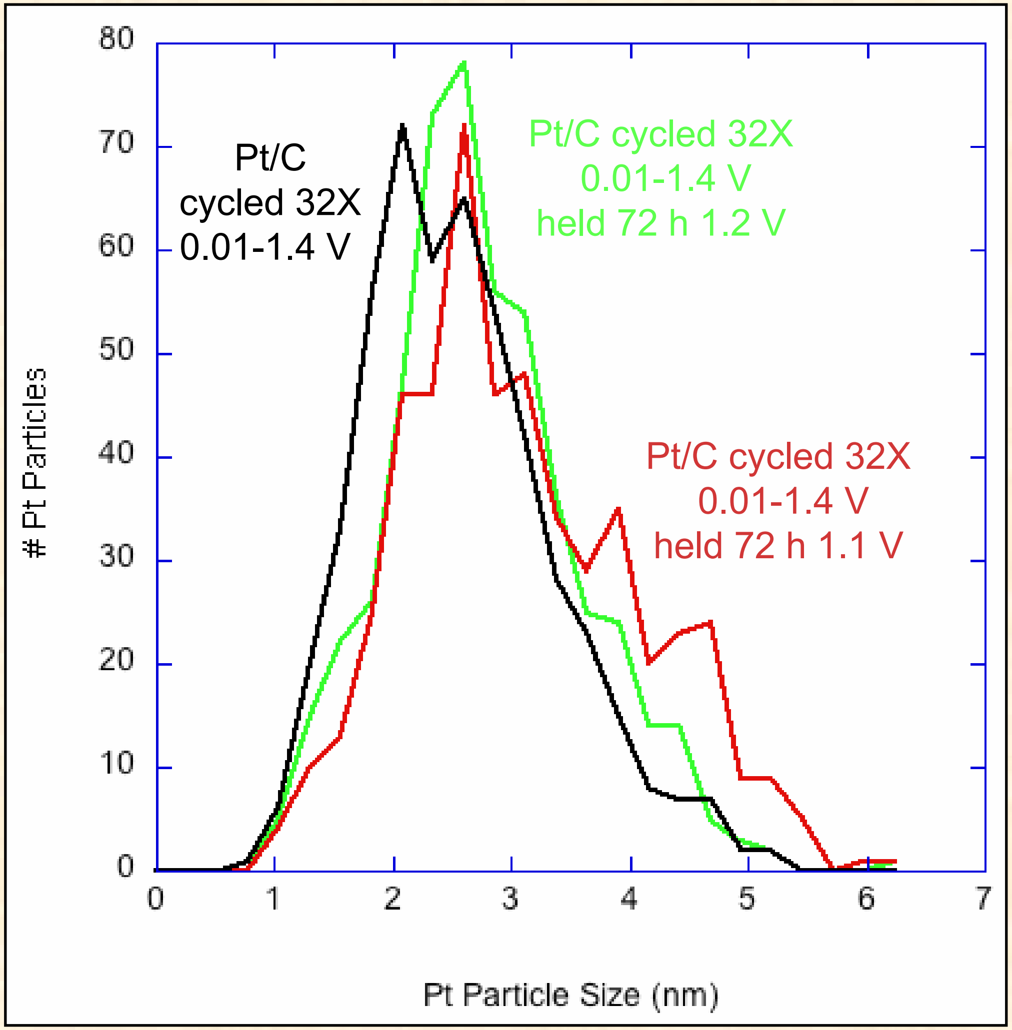
TEM Used to Evaluate Pt Particle Size Changes

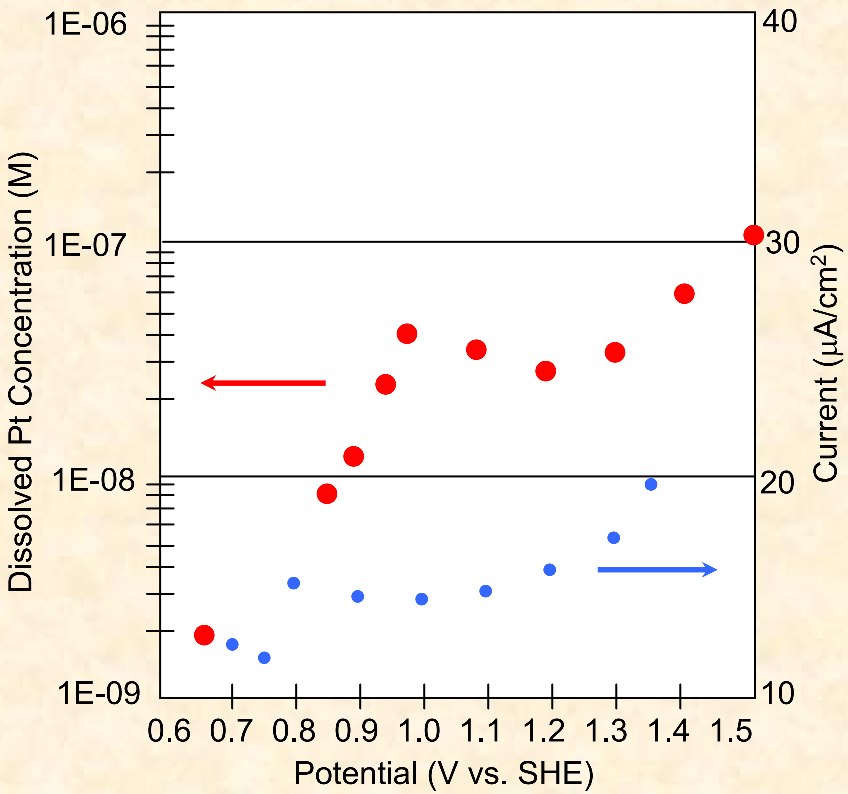




Electrochemical Treatment	Normalized EASA	Pt dissolved	
		ng/cm^2	monolayers
Cycled 0.01-1.4 V	1.0	-	-
Cycled 0.01-1.4 V held 72h @ 1.1 V	0.96	2.3	4.6×10^{-3}
Cycled 0.01-1.4 V held 72h @ 1.2 V	0.91	1.7	3.5×10^{-3}

TEM Used to Evaluate Pt Particle Size Changes





Pt particle size changes were small, but followed same trend as experimental data.

Additional STEM characterization of Pt in ionomer necessary.

Future Work

- Apply the HAADF STEM imaging technique to fresh and electrochemically-aged MEAs in addition to new bi-metallic catalysts. This technique will be especially useful for identifying species migration within the cathode and into the membrane.
- Characterize carbon support microstructural degradation (this has proved to be a difficult challenge because of the recast ionomer in electrodes!)
- Continue to establish collaborations with industries, universities, and national laboratories (including access to ORNL User Facilities) to facilitate "transfer" of unique capabilities.
- Support new DOE projects with microstructural characterization and technique development.

Summary

- The HAADF STEM (Z-contrast) imaging technique has been used to characterize the degree of atomic ordering in numerous Pt-based bimetallic catalyst systems:
  - Pt-Co catalyst shows mostly disordered Pt-Co alloy particles, with some ordered Pt_3Co particles and (Pt_3Co/Pt-Co) particles observed in the distribution. Pt-Co had a much larger particle size that Pt-only and a wider particle size distribution
  - Pt_3Cr catalyst particles are highly ordered (nearly 100% of particles) with a very uniform size distribution
  - Pt-W had a very narrow particle size distribution with particles <2.0 nm; much of the Pt-W remained atomically dispersed on the carbon support surface and did not assemble into crystalline particles.
  - Bimetallic catalyst systems also being evaluated include Pt-Ti and Pt-Ru
- Amount of %RH has a similar effect on EASA loss of Pt-Co as observed for Pt-only cathode catalysts, but to a much lesser degree
- Small Pt particle size differences observed for cycled/held ANL samples, but additional work should be done to image Pt within ionomer using HAADF imaging